

## Measuring enthalpy changes

### EXOTHERMIC AND ENDOTHERMIC REACTIONS

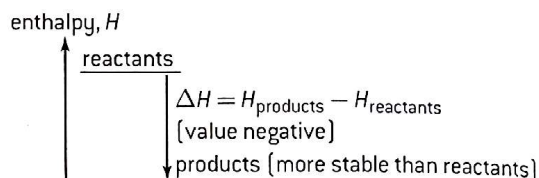
Energy is defined as the ability to do work, that is, move a force through a distance. It is measured in joules.

$$\text{Energy} = \text{force} \times \text{distance}$$

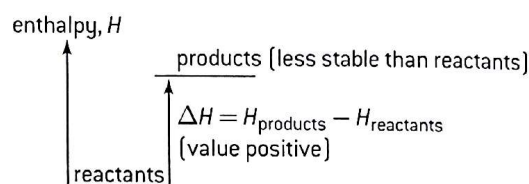
$$(\text{J}) \quad (\text{N} \times \text{m})$$

In a chemical reaction energy is required to break the bonds in the reactants, and energy is given out when new bonds are formed in the products. The most important type of energy in chemistry is heat. If the bonds in the products are stronger than the bonds in the reactants then the reaction is said to be **exothermic**, as heat is given out to the surroundings. Examples of exothermic processes include combustion and neutralization. In **endothermic** reactions heat is absorbed from the surroundings because the bonds in the reactants are stronger than the bonds in the products.

The internal energy stored in the reactants is known as its **enthalpy**,  $H$ . The absolute value of the enthalpy of the reactants cannot be known, nor can the enthalpy of the products, but what can be measured is the difference between them,  $\Delta H$ . By convention  $\Delta H$  has a negative value for exothermic reactions and a positive value for endothermic reactions. It is normally measured under standard conditions of 100 kPa pressure at a temperature of 298 K. The **standard enthalpy change of a reaction** is denoted by  $\Delta H^\ominus$ .



Representation of exothermic reaction using an enthalpy diagram.

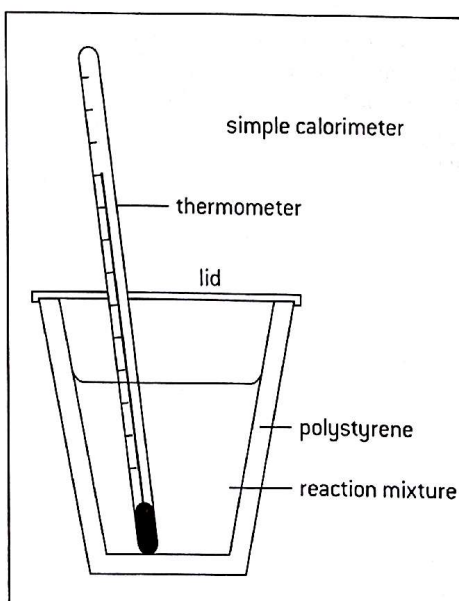
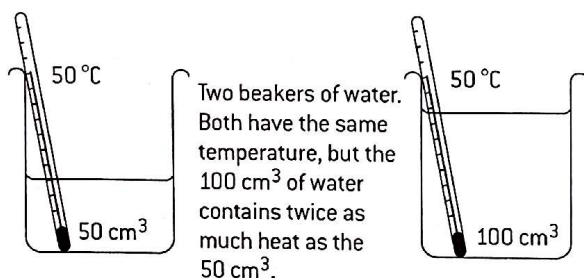


Representation of endothermic reaction using an enthalpy diagram.

### TEMPERATURE AND HEAT

It is important to be able to distinguish between heat and temperature as the terms are often used loosely.

- Heat is a measure of the total energy in a given amount of substance and therefore depends on the amount of substance present.
- Temperature is a measure of the 'hotness' of a substance. It represents the average kinetic energy of the substance, but is independent of the amount of substance present.



### CALORIMETRY

The enthalpy change for a reaction can be measured experimentally by using a calorimeter. In a simple calorimeter all the heat evolved in an exothermic reaction is used to raise the temperature of a known mass of water. For endothermic reactions the heat transferred from the water to the reaction can be calculated by measuring the lowering of temperature of a known mass of water.

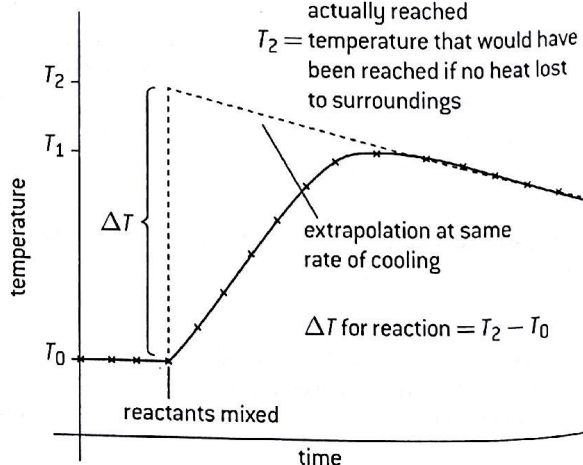
To compensate for heat lost by the water in exothermic reactions to the surroundings as the reaction proceeds a plot of temperature against time can be drawn. By extrapolating the graph, the temperature rise that would have taken place had the reaction been instantaneous can be calculated.

#### Compensating for heat lost

$T_0$  = initial temperature of reactants

$T_1$  = highest temperature actually reached

$T_2$  = temperature that would have been reached if no heat lost to surroundings



# $\Delta H$ calculations

## CALCULATION OF ENTHALPY CHANGES

The heat involved in changing the temperature of any substance can be calculated from the equation:

$$\text{Heat energy} = \text{mass } (m) \times \text{specific heat capacity } (c) \times \text{temperature change } (\Delta T)$$

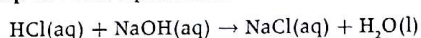
The specific heat capacity of water is  $4.18 \text{ kJ kg}^{-1} \text{ K}^{-1}$ . That is, it requires 4.18 kilojoules of energy to raise the temperature of one kilogram of water by one kelvin.

Enthalpy changes are normally quoted in  $\text{kJ mol}^{-1}$ , for either a reactant or a product, so it is also necessary to work out the number of moles involved in the reaction which produces the heat change in the water.

### WORKED EXAMPLE 1

$50.0 \text{ cm}^3$  of  $1.00 \text{ mol dm}^{-3}$  hydrochloric acid solution was added to  $50.0 \text{ cm}^3$  of  $1.00 \text{ mol dm}^{-3}$  sodium hydroxide solution in a polystyrene beaker. The initial temperature of both solutions was  $16.7^\circ\text{C}$ . After stirring and accounting for heat loss the highest temperature reached was  $23.5^\circ\text{C}$ . Calculate the enthalpy change for this reaction.

**Step 1.** Write equation for reaction



**Step 2.** Calculate molar quantities

$$\text{Amount of HCl} = \frac{50.0}{1000} \times 1.00 = 5.00 \times 10^{-2} \text{ mol}$$

$$\text{Amount of NaOH} = \frac{50.0}{1000} \times 1.00 = 5.00 \times 10^{-2} \text{ mol}$$

Therefore the heat evolved will be for  $5.00 \times 10^{-2} \text{ mol}$

**Step 3.** Calculate heat evolved

Total volume of solution =  $50.0 + 50.0 = 100 \text{ cm}^3$

Assume the solution has the same density and specific heat capacity as water then

mass of 'water' =  $100 \text{ g} = 0.100 \text{ kg}$

Temperature change =  $23.5 - 16.7 = 6.8^\circ\text{C} = 6.8 \text{ K}$

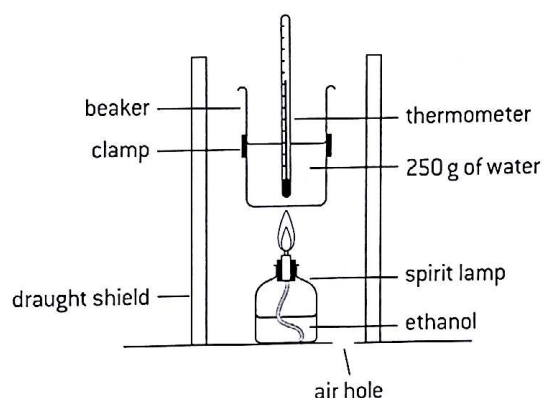
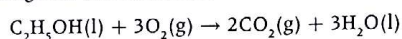
$$\begin{aligned} \text{Heat evolved in reaction} &= 0.100 \times 4.18 \times 6.8 = 2.84 \text{ kJ} \\ &= 2.84 \text{ kJ (for } 5.00 \times 10^{-2} \text{ mol)} \end{aligned}$$

$$\Delta H \text{ for reaction} = -2.84 \times \frac{1}{5.00 \times 10^{-2}} = -56.8 \text{ kJ mol}^{-1}$$

(negative value as the reaction is exothermic)

### WORKED EXAMPLE 2

A student used a simple calorimeter to determine the enthalpy change for the combustion of ethanol.



When  $0.690 \text{ g}$  ( $0.015 \text{ mol}$ ) of ethanol was burned it produced a temperature rise of  $13.2 \text{ K}$  in  $250 \text{ g}$  of water. Calculate  $\Delta H$  for the reaction.

$$\begin{aligned} \text{Heat evolved} \\ \text{by } 0.015 \text{ mol} &= \frac{250}{1000} \times 4.18 \times 13.2 = 13.79 \text{ kJ} \end{aligned}$$

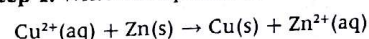
$$\Delta H = -13.79 \times \frac{1}{0.015} = -920 \text{ kJ mol}^{-1}$$

Note: the IB data booklet value is  $-1371 \text{ kJ mol}^{-1}$ . Reasons for the discrepancy include the fact that not all the heat produced is transferred to the water, the water loses some heat to the surroundings, and there is incomplete combustion of the ethanol.

### WORKED EXAMPLE 3

$50.0 \text{ cm}^3$  of  $0.200 \text{ mol dm}^{-3}$  copper(II) sulfate solution was placed in a polystyrene cup. After two minutes  $1.20 \text{ g}$  of powdered zinc was added. The temperature was taken every 30 seconds and the following graph obtained. Calculate the enthalpy change for the reaction taking place.

**Step 1.** Write the equation for the reaction



**Step 2.** Determine the limiting reagent

$$\text{Amount of Cu}^{2+}\text{(aq)} = \frac{50.0}{1000} \times 0.200 = 0.0100 \text{ mol}$$

$$\text{Amount of Zn(s)} = \frac{1.20}{65.37} = 0.0184 \text{ mol}$$

$\therefore \text{Cu}^{2+}\text{(aq)}$  is the limiting reagent

**Step 3.** Extrapolate the graph (already done) to compensate for heat loss and determine  $\Delta T$

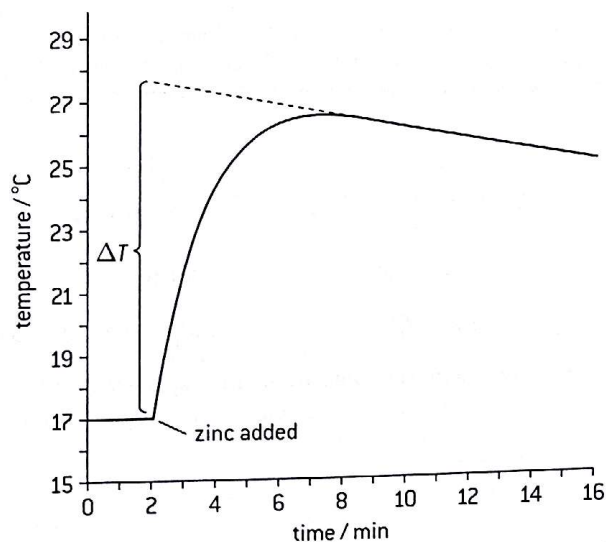
$$\Delta T = 10.4^\circ\text{C}$$

**Step 4.** Calculate the heat evolved in the experiment for  $0.0100 \text{ mol}$  of reactants

$$\text{Heat evolved} = \frac{50.0}{1000} \times 4.18 \times 10.4^\circ\text{C} = 2.17 \text{ kJ}$$

**Step 5.** Express this as the enthalpy change for the reaction

$$\Delta H = -2.17 \times \frac{1}{0.0100} = -217 \text{ kJ mol}^{-1}$$



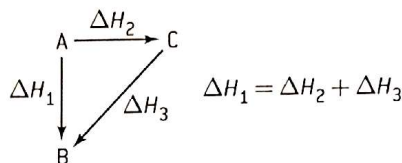


# Hess' Law and standard enthalpy changes

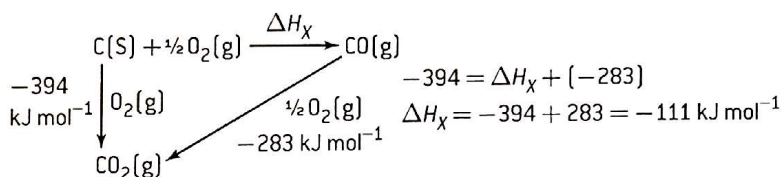
## HESS' LAW

Hess' law states that the enthalpy change for a reaction depends only on the difference between the enthalpy of the products and the enthalpy of the reactants. It is independent of the reaction pathway.

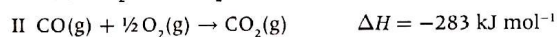
The enthalpy change going from A to B is the same whether the reaction proceeds directly to B or whether it goes via an intermediate.



This law is a statement of the law of conservation of energy. It can be used to determine enthalpy changes, which cannot be measured directly. For example, the enthalpy of combustion of both carbon and carbon monoxide to form carbon dioxide can easily be measured directly, but the combustion of carbon to carbon monoxide cannot. This can be represented by an energy cycle.



Hess' law problems can also be solved by using simultaneous equations. Write the equations that are known and then manipulate them to arrive at the required equation. For example,



Subtract II from I



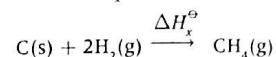
Rearrange equation



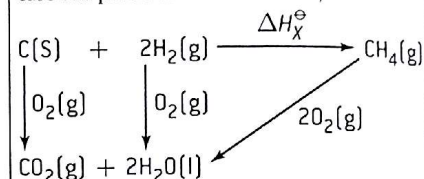
## WORKED EXAMPLE

Calculate the standard enthalpy change when one mole of methane is formed from its elements in their standard states. The standard enthalpies of combustion  $\Delta H_c^\ominus$  of carbon, hydrogen, and methane are  $-394$ ,  $-286$ , and  $-890 \text{ kJ mol}^{-1}$  respectively.

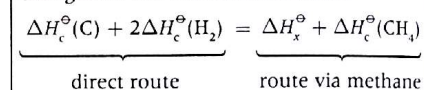
**Step 1.** Write the equation for the enthalpy change with the unknown  $\Delta H_x^\ominus$  value. Call this value  $\Delta H_x^\ominus$



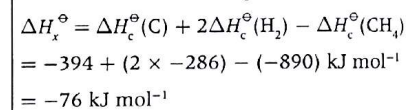
**Step 2.** Construct an energy cycle showing the different routes to the products (in this case the products of combustion)



**Step 3.** Use Hess' law to equate the energy changes for the two different routes



**Step 4.** Rearrange the equation and substitute the values to give the answer

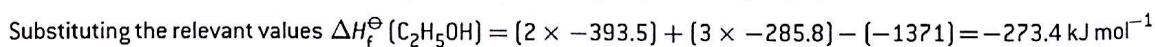
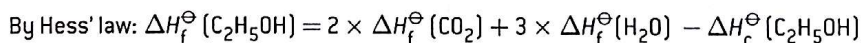
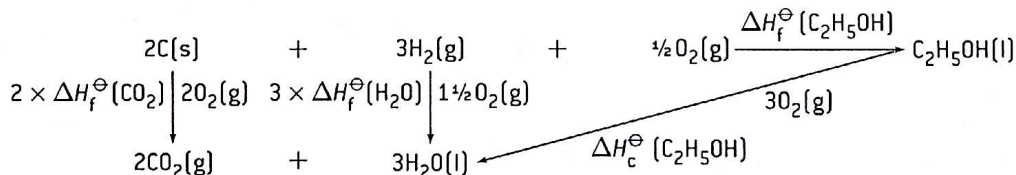


## STANDARD ENTHALPY CHANGES OF FORMATION $\Delta H_f^\ominus$ AND COMBUSTION $\Delta H_c^\ominus$

The standard enthalpy change of formation of a compound is the enthalpy change when one mole of the compound is formed from its elements in their standard states at 298 K and 100 kPa pressure. From this it follows that  $\Delta H_f^\ominus$  for an element in its standard state will be zero. The standard enthalpy change of combustion,  $\Delta H_c^\ominus$ , is the enthalpy change when one mole of a substance is completely combusted in oxygen under standard conditions (298 K and 100 kPa pressure).

## APPLICATION OF HESS' LAW

The standard enthalpy change of formation of ethanol,  $\text{C}_2\text{H}_5\text{OH(l)}$  cannot be determined directly but an accurate value can be obtained indirectly by using the experimental values (in  $\text{kJ mol}^{-1}$ ) for the standard enthalpy changes of combustion of carbon ( $-393.5$ ), hydrogen ( $-285.8$ ) and ethanol ( $-1371$ ). Although this could be solved by just using simultaneous equations it is neater to show the energy cycle. Hess' law is then applied by equating the energy changes involved in combusting carbon and hydrogen directly with the energy changes involved when they are first combined to form ethanol and then combusting the ethanol.



# Bond enthalpies

## BOND ENTHALPIES

Enthalpy changes can also be calculated directly from bond enthalpies. The bond enthalpy is defined as the enthalpy change for the process



For bond formation the value is negative as energy is evolved and for bond breaking energy has to be put in so the value is positive. For simple diatomic molecules where there are only two atoms the values can be known precisely. However for bonds such as the C-H bond there are many compounds containing a C-H bond and the value can differ slightly depending upon the surrounding atoms. The term **average bond enthalpy** is used. This is defined as the energy needed to break one mole of a bond in a gaseous molecule averaged over similar compounds.

If the bond enthalpy values are known for all the bonds in the reactants and products then the overall enthalpy change can be calculated.

### Some bond enthalpies and average bond enthalpies

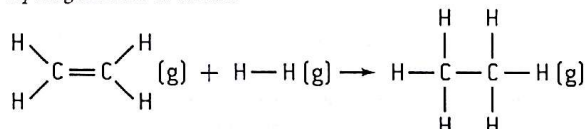
All values in  $\text{kJ mol}^{-1}$

H-H	436	C=C	614	C≡C	839
C-C	346	O=O	498	N≡N	945
C-H	414				
O-H	463				
N-H	391				
N-N	158				

Note that the O=O bond is stronger in  $\text{O}_2$  than the O-O bond in ozone,  $\text{O}_3$ , ( $362 \text{ kJ mol}^{-1}$ ). This is important as the ozone layer protects the Earth from damaging ultraviolet radiation by absorbing both high and low energy uv light to break these bonds (see *Importance of the ozone layer* on page 33).

## WORKED EXAMPLE 1

Hydrogenation of ethene



energy absorbed to  
break bonds:

$$\begin{array}{l} \text{C}=\text{C} \quad 614 \\ 4 \text{ C}-\text{H} \quad 4 \times 414 \\ \text{H}-\text{H} \quad 436 \end{array} \left. \vphantom{\begin{array}{l} \text{C}=\text{C} \\ 4 \text{ C}-\text{H} \\ \text{H}-\text{H} \end{array}} \right\} 2706 \text{ kJ}$$

energy released when  
bonds are formed:

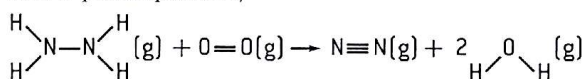
$$\begin{array}{l} \text{C}-\text{C} \quad 346 \\ 6 \text{ C}-\text{H} \quad 6 \times 414 \end{array} \left. \vphantom{\begin{array}{l} \text{C}-\text{C} \\ 6 \text{ C}-\text{H} \end{array}} \right\} 2830 \text{ kJ}$$

There is more energy released than absorbed so the reaction is exothermic.

$$\Delta H = -(2830 - 2706) = -124 \text{ kJ mol}^{-1}$$

## WORKED EXAMPLE 2

Combustion of hydrazine in oxygen (this reaction has been used to power spacecraft)



energy absorbed:

$$\begin{array}{l} \text{N}-\text{N} \quad 158 \\ 4 \text{ N}-\text{H} \quad 4 \times 391 \\ \text{O}=\text{O} \quad 498 \end{array} \left. \vphantom{\begin{array}{l} \text{N}-\text{N} \\ 4 \text{ N}-\text{H} \\ \text{O}=\text{O} \end{array}} \right\} 2220$$

energy released:

$$\begin{array}{l} \text{N}\equiv\text{N} \quad 945 \\ 4 \text{ O}-\text{H} \quad 4 \times 463 \end{array} \left. \vphantom{\begin{array}{l} \text{N}\equiv\text{N} \\ 4 \text{ O}-\text{H} \end{array}} \right\} 2797$$

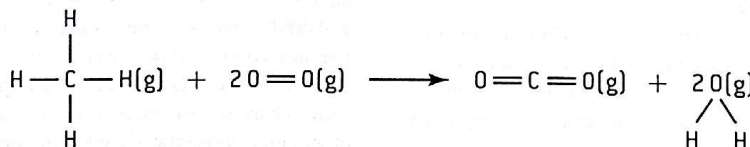
$$\Delta H = -(2797 - 2220) = -577 \text{ kJ mol}^{-1}$$

## LIMITATIONS OF USING BOND ENTHALPIES

Bond enthalpies can only be used on their own if all the reactants and products are in the gaseous state. If water were a liquid product in the above example then even more heat would be evolved since the enthalpy change of vaporization of water would also be needed to be included in the calculation.

In the above calculations some average bond enthalpies have been used. These have been obtained by considering a number of similar compounds containing the bond in question. In practice the energy of a particular bond will vary in different compounds. For this reason  $\Delta H$  values obtained from using bond enthalpies will not necessarily be very accurate. Both these points are illustrated by the determination of the enthalpy change of combustion of methane by using bond enthalpies.

The equation for the reaction using bond enthalpies is:



$$\Delta H_{\text{reaction}} = \Sigma(\Delta H_f \text{ products}) - \Sigma(\Delta H_f \text{ reactants})$$

Energy taken in /  $\text{kJ mol}^{-1}$

$$4 \times \text{C}-\text{H} = 4 \times 414 = +1656$$

$$2 \times \text{O}=\text{O} = 2 \times 498 = +996$$

$$\text{Total} = +2652$$

Energy given out /  $\text{kJ mol}^{-1}$

$$2 \times \text{C}=\text{O} = 2 \times (-804) = -1608$$

$$4 \times \text{O}-\text{H} = 4 \times (-463) = -1852$$

$$\text{Total} = -3468$$

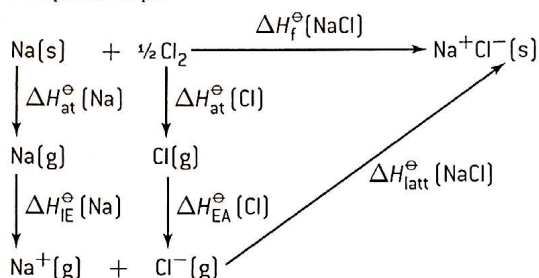
The calculated enthalpy change for the reaction using bond enthalpies is therefore equal to  $-816 \text{ kJ mol}^{-1}$ . However this is considerably different to the value of  $-891 \text{ kJ mol}^{-1}$  given in Section 13 of the IB data booklet. It is to be expected that there will be a difference as the definition of enthalpy of combustion is that the reactants and products should be in their normal states under standard conditions so we need to consider the extra  $2 \times 44 \text{ kJ mol}^{-1}$  of energy given out when the two moles of gaseous water product turn to liquid water. This will now bring the enthalpy of combustion value to  $-904 \text{ kJ mol}^{-1}$ . This is much closer to  $-891 \text{ kJ mol}^{-1}$  with a difference of about 1.5%. This difference is due to the fact that average bond enthalpies have been used throughout and the fact that the bond enthalpy for C=O in carbon dioxide, where there are two double bonds to oxygen on the same carbon atom, may be different to the average C=O enthalpy.



# HL Energy cycles

## BORN-HABER CYCLES

Born-Haber cycles are simply energy cycles for the formation of ionic compounds. The enthalpy change of formation of sodium chloride can be considered to occur through a number of separate steps.



Using Hess' law:

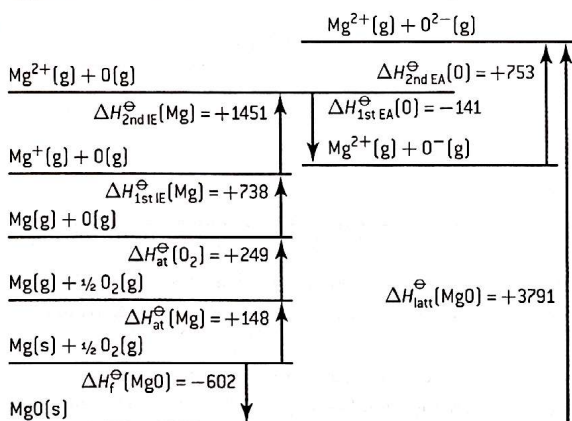
$$\Delta H_f^\ominus(\text{NaCl}) = \Delta H_{\text{at}}^\ominus(\text{Na}) + \Delta H_{\text{IE}}^\ominus(\text{Na}) + \Delta H_{\text{at}}^\ominus(\text{Cl}) + \Delta H_{\text{EA}}^\ominus(\text{Cl}) + \Delta H_{\text{latt}}^\ominus(\text{NaCl})$$

Substituting the relevant values:

$$\Delta H_f^\ominus(\text{NaCl}) = +108 + 496 + 121 - 349 - 790 = -414 \text{ kJ mol}^{-1}$$

Note: it is the large lattice enthalpy that mainly compensates for the endothermic processes and leads to the enthalpy of formation of ionic compounds having a negative value.

Sometimes Born-Haber cycles are written as energy level diagrams with the arrows for endothermic processes in the opposite direction to the arrows for exothermic processes.



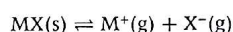
## ENTHALPY OF ATOMIZATION

The standard enthalpy of atomization is the standard enthalpy change when one mole of gaseous atoms is formed from the element in its standard state under standard conditions. For diatomic molecules this is equal to half the bond dissociation enthalpy.



## LATTICE ENTHALPY

The lattice enthalpy relates either to the endothermic process of turning a crystalline solid into its gaseous ions or to the exothermic process of turning gaseous ions into a crystalline solid.



The sign of the lattice enthalpy indicates whether the lattice is being formed (-) or broken (+).

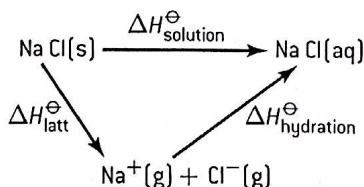
The size of the lattice enthalpy depends both on the size of the ions and on the charge carried by the ions.

The smaller the ion and the greater the charge, the higher the lattice enthalpy.

cation size increasing			anion size increasing		
LiCl	NaCl	KCl	NaCl	NaBr	NaI
Lattice enthalpy / kJ mol <sup>-1</sup>					
864	790	720	790	754	705
charge on cation increasing			charge on anion increasing		
NaCl	MgCl <sub>2</sub>		MgCl <sub>2</sub>	MgO	
Lattice enthalpy / kJ mol <sup>-1</sup>					
790	2540		2540	3791	

## SOLUBILITY OF SALTS

It takes considerable energy to melt sodium chloride (melting point 801 °C) due to the strong electrostatic attractions in its lattice and yet the lattice can easily be broken down by dissolving salt in water at room temperature. An energy cycle can be drawn to explain why.



The overall step is known as the enthalpy change of solution – the enthalpy change when 1 mole of an ionic substance dissolves in water to give a solution of infinite dilution. This can be considered to proceed in two stages. The first involves the lattice enthalpy to break the lattice into gaseous ions, which will be highly endothermic and the second to hydrate the gaseous ions into

aqueous ions. This second step is known as the **hydration energy** and can be defined as the enthalpy change when 1 mole of gaseous ions dissolves in sufficient water to give an infinitely dilute solution. It is a highly exothermic process. Generally the smaller and more highly charged the ion the greater the hydration energy. In the case of sodium chloride the value for the sum of the hydration energies of the Na<sup>+</sup> and Cl<sup>-</sup> ions is very similar to the lattice enthalpy of NaCl and the small difference of about 7 kJ mol<sup>-1</sup> can be made up by taking some heat from the water so it dissolves with a slight lowering of temperature.

$$\Delta H_{\text{solution}}^\ominus = \Delta H_{\text{latt}}^\ominus + \Delta H_{\text{hydration}}^\ominus = +790 + (-783) = +7 \text{ kJ mol}^{-1}$$

Whether or not other salts are soluble in water depends upon the relative size of the lattice enthalpy compared with the hydration energy. The highly exothermic nature of hydration energy can explain why it is inadvisable to add water to sulfur trioxide. As sulfur trioxide is not ionic there is no strong lattice enthalpy to overcome and the hydration energy released as heat is so strong that the resulting sulfuric acid can boil.

# HL Entropy and spontaneity

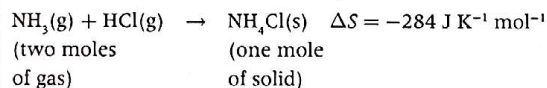
## ENTROPY

Entropy ( $S$ ) refers to the distribution of available energy among the particles in a system. The more ways the energy can be distributed the higher the entropy. This is sometimes equated to a measure of the disorder of a system. In nature, systems naturally tend towards an increase in entropy. An increase in entropy (disorder) can result from:

- mixing different types of particles, e.g. the dissolving of sugar in water
- a change in state where the distance between the particles increases, e.g. liquid water  $\rightarrow$  steam
- the increased movement of particles, e.g. heating a liquid or gas
- increasing the number of particles, e.g.  
 $2\text{H}_2\text{O}_2(\text{l}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$ .

The greatest increase in disorder is usually found where the number of particles in the gaseous state increases.

The change in the disorder of a system is known as the entropy change,  $\Delta S$ . The more disordered the system becomes the more positive the value of  $\Delta S$  becomes. Systems which become more ordered will have negative  $\Delta S$  values.



## SPONTANEITY

A reaction is said to be spontaneous if it causes a system to move from a less stable to a more stable state. This will depend both upon the enthalpy change and the entropy change. These two factors can be combined and expressed as the Gibbs energy change  $\Delta G$ , often known as the 'free energy change'.

The standard free energy change  $\Delta G^\ominus$  is defined as:

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

where all the values are measured under standard conditions.

For a reaction to be spontaneous it must be able to do work, that is  $\Delta G^\ominus$  must have a negative value.

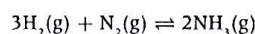
Note: the fact that a reaction is spontaneous does not necessarily mean that it will proceed without any input of energy. For example, the combustion of coal is a spontaneous reaction and yet coal is stable in air. It will only burn on its own accord after it has received some initial energy so that some of the molecules have the necessary activation energy for the reaction to occur.

## ABSOLUTE ENTROPY VALUES

The standard entropy of a substance is the entropy change per mole that results from heating the substance from 0 K to the standard temperature of 298 K. Unlike enthalpy, absolute values of entropy can be measured. The standard entropy change for a reaction can then be determined by calculating the difference between the entropy of the products and the reactants.

$$\Delta S^\ominus = S^\ominus (\text{products}) - S^\ominus (\text{reactants})$$

e.g. for the formation of ammonia



the standard entropies of hydrogen, nitrogen and ammonia are respectively 131, 192 and 192  $\text{J K}^{-1} \text{ mol}^{-1}$ .

Therefore per mole of reaction

$$\Delta S^\ominus = 2 \times 192 - [(3 \times 131) + 192] = -201 \text{ J K}^{-1} \text{ mol}^{-1}$$

(or per mole of ammonia  $\Delta S^\ominus = \frac{-201}{2} = -101 \text{ J K}^{-1} \text{ mol}^{-1}$ )

## FREE ENERGY, $\Delta G^\ominus$ , AND THE POSITION OF EQUILIBRIUM

As a reaction proceeds, the composition of the reactants and products is continually changing and the free energy will also be changing. The position of equilibrium corresponds to a maximum value of entropy and a minimum in the value of the Gibbs free energy change. The reaction will not proceed any further at this point, i.e. the rate of the forward reaction will equal the rate of the reverse reaction. The equilibrium composition of an equilibrium mixture thus depends upon the value of  $\Delta G^\ominus$ . From this it can also be deduced that the equilibrium constant for the reaction,  $K_c$ , will also depend upon the value of  $\Delta G^\ominus$  (see page 56).



# HL Spontaneity of a reaction

## POSSIBLE COMBINATIONS FOR FREE ENERGY CHANGES

Some reactions will always be spontaneous. If  $\Delta H^\circ$  is negative or zero and  $\Delta S^\circ$  is positive then  $\Delta G^\circ$  must always have a negative value. Conversely if  $\Delta H^\circ$  is positive or zero and  $\Delta S^\circ$  is negative then  $\Delta G^\circ$  must always be positive and the reaction will never be spontaneous.

For some reactions whether or not they will be spontaneous depends upon the temperature. If  $\Delta H^\circ$  is positive or zero and  $\Delta S^\circ$  is positive, then  $\Delta G^\circ$  will only become negative at high temperatures when the value of  $T\Delta S^\circ$  exceeds the value of  $\Delta H^\circ$ .

Type	$\Delta H^\circ$	$\Delta S^\circ$	$T\Delta S^\circ$	$\Delta H^\circ - T\Delta S^\circ$	$\Delta G^\circ$
1	0	+	+	(0) - (+)	-
2	0	-	-	(0) - (-)	+
3	-	+	+	(-) - (+)	-
4	+	-	-	(+) - (-)	+
5	+	+	+	(+) - (+)	- or +
6	-	-	-	(-) - (-)	+ or -

**Type 1.** Mixing two gases.  $\Delta G^\circ$  is negative so gases will mix of their own accord. Gases do not unmix of their own accord (Type 2) as  $\Delta G^\circ$  is positive.

**Type 3.**  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7(\text{s}) \rightarrow \text{N}_2(\text{g}) + \text{Cr}_2\text{O}_3(\text{s}) + 4\text{H}_2\text{O}(\text{g})$

The decomposition of ammonium dichromate is spontaneous at all temperatures.

**Type 4.**  $\text{N}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{N}_2\text{H}_4(\text{g})$

The formation of hydrazine from its elements will never be spontaneous.

**Type 5.**  $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

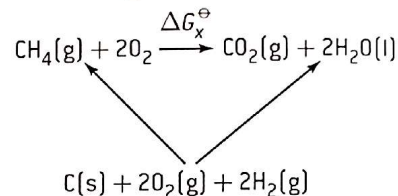
The decomposition of calcium carbonate is only spontaneous at high temperatures.

**Type 6.**  $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$

Above a certain temperature this reaction will cease to be spontaneous.

## DETERMINING THE VALUE OF $\Delta G^\circ$

The precise value of  $\Delta G^\circ$  for a reaction can be determined from  $\Delta G_f^\circ$  values using an energy cycle, e.g. to find the standard free energy of combustion of methane given the standard free energies of formation of methane, carbon dioxide, water, and oxygen.



By Hess' law

$$\Delta G_x^\circ = [\Delta G_f^\circ(\text{CO}_2) + 2\Delta G_f^\circ(\text{H}_2\text{O})] - [\Delta G_f^\circ(\text{CH}_4) + 2\Delta G_f^\circ(\text{O}_2)]$$

Substituting the actual values

$$\Delta G_x^\circ = [-394 + 2 \times (-237)] - [-50 + 2 \times 0] = -818 \text{ kJ mol}^{-1}$$

$\Delta G^\circ$  values can also be calculated from using the equation  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ . For example, in Type 5 in the adjacent list the values for  $\Delta H^\circ$  and  $\Delta S^\circ$  for the thermal decomposition of calcium carbonate are  $+178 \text{ kJ mol}^{-1}$  and  $+165.3 \text{ J K}^{-1} \text{ mol}^{-1}$  respectively. Note that the units of  $\Delta S^\circ$  are different to those of  $\Delta H^\circ$ .

$$\text{At } 25^\circ\text{C (298 K) the value for } \Delta G^\circ = 178 - 298 \times \frac{165.3}{1000} = +129 \text{ kJ mol}^{-1}$$

which means that the reaction is not spontaneous.

The reaction will become spontaneous when  $T\Delta S^\circ > \Delta H^\circ$ .

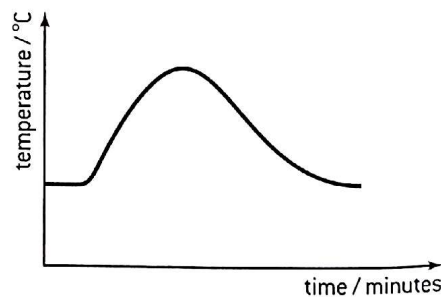
$$T\Delta S^\circ = \Delta H^\circ \text{ when } T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{178}{165.3/1000} = 1077 \text{ K (804}^\circ\text{C)}$$

Therefore above  $804^\circ\text{C}$  the reaction will be spontaneous.

Note: this calculation assumes that the entropy value is independent of temperature, which is not strictly true.

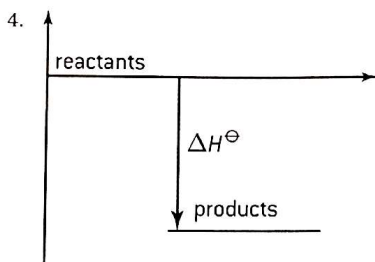
## MULTIPLE CHOICE QUESTIONS – ENERGETICS / THERMOCHEMISTRY

- Which statement about the reaction below is correct?  
 $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) \quad \Delta H^\circ = -114 \text{ kJ}$ 
  - 114 kJ of energy are absorbed for every mole of NO reacted.
  - 114 kJ of energy are released for every mole of NO reacted.
  - 57 kJ of energy are absorbed for every mole of NO reacted.
  - 57 kJ of energy are released for every mole of NO reacted.
- When an aqueous solution of sulfuric acid is added to an aqueous solution of potassium hydroxide the temperature increases. Which describes the reaction taking place?
- A student measured the temperature of a reaction mixture over time using a temperature probe. By considering the graph, which of the following deductions can be made?



- The reaction is exothermic.
  - The products are more stable than the reactants.
  - The reactant bonds are stronger than the product bonds.
- I and II only
  - I and III only
  - II and III only
  - I, II and III

	Type	Sign of $\Delta H^\circ$
A.	Exothermic	+
B.	Exothermic	-
C.	Endothermic	-
D.	Endothermic	+



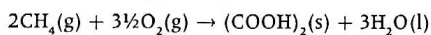
What can be deduced about the relative stability of the reactants and products and the sign of  $\Delta H^\ominus$ , from the enthalpy level diagram above?

**Relative stability**

**Sign of  $\Delta H^\ominus$**

- |                          |   |
|--------------------------|---|
| A. Products more stable  | - |
| B. Products more stable  | + |
| C. Reactants more stable | - |
| D. Reactants more stable | + |
5. Consider the following reactions.
- |  |                        |
|--|------------------------|
| $\text{CH}_4(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{HCHO}(\text{l}) + \text{H}_2\text{O}(\text{l})$                  | $\Delta H^\ominus = x$ |
| $\text{HCHO}(\text{l}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{HCOOH}(\text{l})$                                     | $\Delta H^\ominus = y$ |
| $2\text{HCOOH}(\text{l}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow (\text{COOH})_2(\text{s}) + \text{H}_2\text{O}(\text{l})$ | $\Delta H^\ominus = z$ |

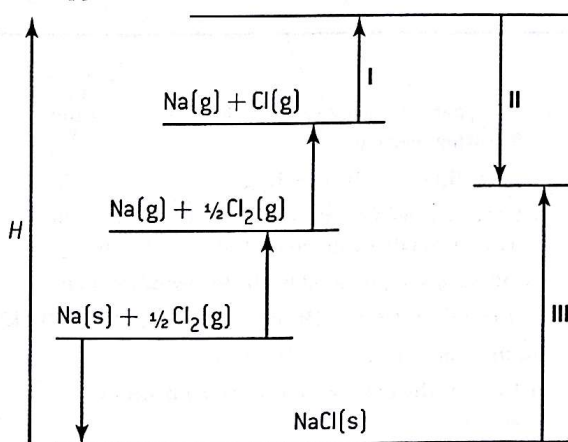
What is the enthalpy change of the reaction below?



- |                 |                   |
|-----------------|-------------------|
| A. $x + y + z$  | C. $2x + 2y + z$  |
| B. $2x + y + z$ | D. $2x + 2y + 2z$ |

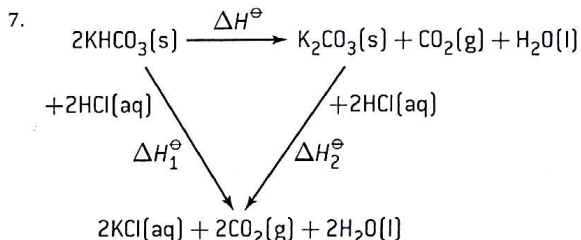


9. Which is a correct definition of lattice enthalpy?
- It is the enthalpy change that occurs when an electron is removed from 1 mol of gaseous atoms.
  - It is the enthalpy change that occurs when 1 mol of a compound is formed from its elements.
  - It is the enthalpy change that occurs when 1 mol of solid crystal changes into a liquid.
  - It is the enthalpy change that occurs when 1 mol of solid crystal is formed from its gaseous ions.
10. The diagram represents the Born-Haber cycle for the lattice enthalpy of sodium chloride.



6. Which equation represents the H-F bond enthalpy?

- $2\text{HF}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{F}_2(\text{g})$
- $\text{HF}(\text{g}) \rightarrow \text{H}^+(\text{g}) + \text{F}^-(\text{g})$
- $\text{HF}(\text{g}) \rightarrow \text{H}^-(\text{g}) + \text{F}^+(\text{g})$
- $\text{HF}(\text{g}) \rightarrow \text{H}(\text{g}) + \text{F}(\text{g})$



This cycle may be used to determine  $\Delta H^\ominus$  for the decomposition of potassium hydrogencarbonate. Which expression can be used to calculate  $\Delta H^\ominus$ ?

- |   |  |
|---|--|
| A. $\Delta H^\ominus = \Delta H_1^\ominus + \Delta H_2^\ominus$ | C. $\Delta H^\ominus = \frac{1}{2}\Delta H_1^\ominus - \Delta H_2^\ominus$ |
| B. $\Delta H^\ominus = \Delta H_1^\ominus - \Delta H_2^\ominus$ | D. $\Delta H^\ominus = \Delta H_2^\ominus - \Delta H_1^\ominus$            |
8. Which process is endothermic?
- $\text{HNO}_3(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaNO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$
  - $\text{Cl}(\text{g}) + \text{e}^- \rightarrow \text{Cl}^-(\text{g})$
  - $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$
  - $\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$

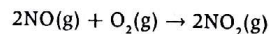
What is the name of the enthalpy changes I, II and III?

	I	II	III
A.	ionization energy of Na	electron affinity of Cl	lattice enthalpy of NaCl
B.	lattice enthalpy of NaCl	ionization energy of Na	electron affinity of Cl
C.	electron affinity of Cl	ionization energy of Na	lattice enthalpy of NaCl
D.	ionization energy of Na	lattice enthalpy of NaCl	electron affinity of Cl

11. Which reaction has the largest increase in entropy?

- $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$
- $\text{Al}(\text{OH})_3(\text{s}) + \text{NaOH}(\text{aq}) \rightarrow \text{Al}(\text{OH})_4^-(\text{aq}) + \text{Na}^+(\text{aq})$
- $\text{Na}_2\text{CO}_3(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow 2\text{NaCl}(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
- $\text{BaCl}_2(\text{aq}) + \text{Na}_2\text{SO}_4(\text{aq}) \rightarrow \text{BaSO}_4(\text{s}) + 2\text{NaCl}(\text{aq})$

12. Which statements about entropy for the following reaction at 298 K are correct?



- $S^\ominus(\text{O}_2) = 0$
- $\Delta S^\ominus = 2S^\ominus(\text{NO}_2) - 2S^\ominus(\text{NO}) - S^\ominus(\text{O}_2)$
- $\Delta S^\ominus < 0$

- |                   |                    |
|-------------------|--------------------|
| A. I and II only  | C. II and III only |
| B. I and III only | D. I, II and III   |



## SHORT ANSWER QUESTIONS – ENERGETICS / THERMOCHEMISTRY

1. In an experiment to measure the enthalpy change of combustion of ethanol, a student heated a copper calorimeter containing 100 cm<sup>3</sup> of water with a spirit lamp and collected the following data.

Initial temperature of water: 20.0 °C

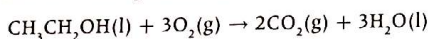
Final temperature of water: 55.0 °C

Mass of ethanol burned: 1.78 g

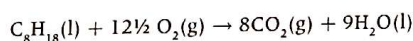
Density of water: 1.00 g cm<sup>-3</sup>

- Use the data to calculate the heat evolved (in kJ) when the ethanol was combusted. [2]
  - Calculate the enthalpy change of combustion per mole of ethanol. [2]
  - Suggest two reasons why the result is not the same as the value in the IB data booklet. [2]
2. Ethanol is used as a component in fuel for some vehicles. One fuel mixture contains 10% by mass of ethanol in unleaded petrol (gasoline). This mixture is often referred to as Gasohol E10.

- a) Assume that the other 90% by mass of Gasohol E10 is octane. 1.00 kg of this fuel mixture was burned.



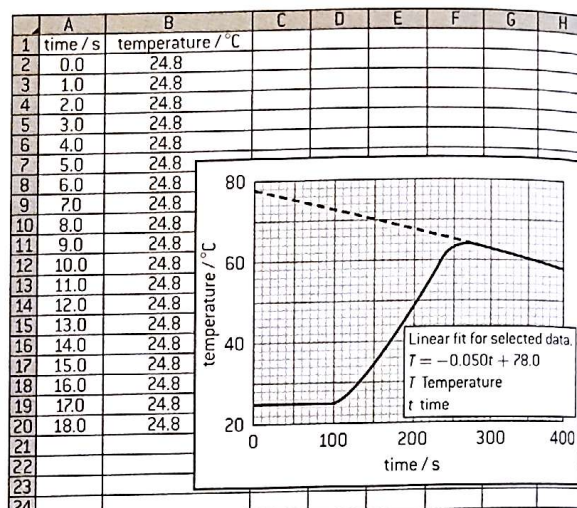
$$\Delta H^\ominus = -1367 \text{ kJ mol}^{-1}$$



$$\Delta H^\ominus = -5470 \text{ kJ mol}^{-1}$$

- Calculate the mass, in g, of ethanol and octane in 1.00 kg of the fuel mixture. [1]
  - Calculate the amount, in mol, of ethanol and octane in 1.00 kg of the fuel mixture. [1]
  - Calculate the total amount of energy, in kJ, released when 1.00 kg of the fuel mixture is completely burned. [3]
- b) If the fuel blend was vaporized before combustion, predict whether the amount of energy released would be greater, less or the same. Explain your answer. [2]
3. The data shown are from an experiment to measure the enthalpy change for the reaction of aqueous copper(II) sulfate, CuSO<sub>4</sub> (aq) and zinc, Zn (s).
- $$\text{Cu}^{2+}\text{(aq)} + \text{Zn (s)} \rightarrow \text{Cu (s)} + \text{Zn}^{2+}\text{(aq)}$$
- 50.0 cm<sup>3</sup> of 1.00 mol dm<sup>-3</sup> copper(II) sulfate solution was placed in a polystyrene cup and zinc powder was added after

100 seconds. The temperature–time data was taken from a data-logging software program. The table shows the initial 19 readings.



A straight line has been drawn through some of the data points. The equation for this line is given by the data-logging software as  $T = -0.050t + 78.0$

The heat produced by the reaction can be calculated from the temperature change,  $\Delta T$ , using the expression  
Heat change = Volume of CuSO<sub>4</sub>(aq) × Specific heat capacity of H<sub>2</sub>O ×  $\Delta T$

- Describe two assumptions made in using this expression to calculate heat changes. [2]
- (i) Use the data presented by the data-logging software to deduce the temperature change,  $\Delta T$ , which would have occurred if the reaction had taken place instantaneously with no heat loss. [2]  
(ii) State the assumption made in part b) (i). [1]  
(iii) Calculate the heat, in kJ, produced during the reaction using the expression given in part a). [1]
- The colour of the solution changed from blue to colourless. Deduce the amount, in moles, of zinc which reacted in the polystyrene cup. [1]
- Calculate the enthalpy change, in kJ mol<sup>-1</sup>, for this reaction. [1]



4. a) The standard enthalpy change of three combustion reactions is given below in kJ.
- $$2\text{C}_2\text{H}_6\text{(g)} + 7\text{O}_2\text{(g)} \rightarrow 4\text{CO}_2\text{(g)} + 6\text{H}_2\text{O(l)} \quad \Delta H^\ominus = -3120$$
- $$2\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{H}_2\text{O(l)} \quad \Delta H^\ominus = -572$$
- $$\text{C}_2\text{H}_4\text{(g)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)} + 2\text{H}_2\text{O(l)} \quad \Delta H^\ominus = -1411$$
- Based on the above information, calculate the standard change in enthalpy,  $\Delta H^\ominus$ , for the following reaction.
- $$\text{C}_2\text{H}_6\text{(g)} \rightarrow \text{C}_2\text{H}_4\text{(g)} + \text{H}_2\text{(g)} \quad [4]$$
- Predict, stating a reason, whether the sign of  $\Delta S^\ominus$  for the above reaction would be positive or negative. [2]
  - Discuss why the above reaction is non-spontaneous at low temperature but becomes spontaneous at high temperatures. [2]

- Using bond enthalpy values, calculate  $\Delta H^\ominus$  for the following reaction. [3]  
$$\text{C}_2\text{H}_6\text{(g)} \rightarrow \text{C}_2\text{H}_4\text{(g)} + \text{H}_2\text{(g)}$$
- Suggest with a reason, why the values obtained in parts a) and d) are different. [1]
- 'Synthesis gas' is produced by the following reaction.  
$$\text{CH}_4\text{(g)} + \text{H}_2\text{O(g)} \rightarrow 3\text{H}_2\text{(g)} + \text{CO(g)} \quad \Delta H^\ominus = +210 \text{ kJ}$$
  
For this reaction  $\Delta S^\ominus = +216 \text{ J K}^{-1}$ .  
  - Explain why this reaction is not spontaneous at 298 K. [2]
  - Calculate the temperature at which this reaction becomes spontaneous. [2]